DOI: 10.1002/ejoc.201000153

Matrix Isolation and IR Characterization of the Benzoyl and Benzoylperoxy Radicals

Artur Mardyukov^[a] and Wolfram Sander*^[a]

Keywords: Radicals / Matrix isolation / IR spectroscopy

The benzoyl radical **1** was synthesized in argon matrices by the thermal reaction of the phenyl radical **2** with CO. The IR spectrum with the C=O str. vibration at 1824.4 cm⁻¹ is in good agreement with DFT calculations. The formation of **1** is reversible and UV irradiation results in the cleavage back to **2**

Introduction

The benzoyl radical **1** is an important reactive intermediate that plays a role in the combustion of aromatic hydrocarbons and as an initiator in polymerization reactions.^[1,2] Aryl ketones are frequently used as photoinitiators in free radical polymerizations.^[3,4] Upon irradiation these ketones undergo Norrish type I cleavage to produce aromatic acyl radicals with high efficiency.^[5–7]



The benzoyl radical **1** has also been proposed to be an intermediate in the combustion of aromatic hydrocarbons. The combustion of aromatic hydrocarbons leads to the formation of the phenyl radical **2** and CO which form an equilibrium with **1**. The thermochemistry and kinetics of the unimolecular decomposition of **1** to give **2** and CO has been studied by Solly and Benson.^[8] At room temperature the reaction enthalpy for the addition reaction was determined to $\Delta H_{298} = -27.5$ kcal/mol with an activation barrier of 2.3 kcal/mol.

Xia and Lin reported precise kinetic data and a reaction enthalpy of -24.6 ± 0.8 kcal/mol using cavity ring-down spectroscopy for this reaction.^[9,10] According to MP2 cal-

WILEY

and CO. The benzoyl radical **1** can react with molecular oxygen in the matrix to produce the benzoylperoxy radical **3**. Radical **3** was also characterized by IR spectroscopy in combination with DFT calculations.

culations the activation barrier for the reaction of **1** with CO is 3.33 kcal/mol while B3LYP predicts a very small activation barrier of only 0.73 kcal/mol.^[10]

The benzoyl radical 1 is highly reactive, and to characterize this radical spectroscopically either low temperature spectroscopy or time resolved spectroscopy (laser flash photolysis LFP) is necessary. Radical 1 was generated in the solid state at 77 K and characterized by EPR spectroscopy.^[11,12] The EPR spectrum could also be obtained by time resolved EPR spectroscopy in solution.^[5] The conclusion of the EPR studies is that the electronic structure of 1 is described best as a σ -radical with an sp² hybridized radical center. A very weak and broad absorption maximum at 650 nm was assigned to the benzoyl radical in an MTHF glass at 77 K.^[13]

The benzoyl radical **1** has also been generated as a transient species in solution at room temperature and investigated by time resolved spectroscopy.^[5,6,14–18] Since its absorptions in the UV/Vis region of the spectrum are only weak, time resolved IR spectroscopy has proven to be particularly useful to detect 1.^[5,6,16,18] The C=O str. vibration of **1** was observed at 1828 cm⁻¹ in *n*-hexane,^[12,16,18,19] at 1824 cm⁻¹ in CCl₄,^[5] and at 1818 cm⁻¹ in acetonitrile.^[6] The lifetime of **1** in solution is in the order of miroseconds, depending on the solvent and the presence of trapping reagents. The reactivity of **1** towards various trapping reagents is similar to that of simple alkyl radicals. If the solution in which **1** is formed contains O₂, the benzoylperoxy radical **3** is rapidly formed with a C=O str. vibration between 1820 and 1814 cm⁻¹, depending on the solvent.^[5,14]

Here, we report the synthesis and IR spectroscopic characterization of the benzoyl radical 1 in an argon matrix. This allows to record the complete mid IR spectrum of 1, which has so far been unknown. The thermal reaction of 1 with molecular oxygen and the photochemistry of the intermediates is also reported.

 [[]a] Lehrstuhl f
ür Organische Chemie II der Ruhr-Universit
ät Bochum 44780 Bochum, Germany

Fax: +49-234-321-4353

E-mail: wolfram.sander@rub.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000153.

Results and Discussion

The Benzoyl Radical

The phenyl radical 2 (Scheme 1) can be easily generated under the conditions of matrix isolation from a variety of thermal and photochemical precursors.^[20–24] To investigate bimolecular reactions of matrix isolated 2 it proved to be advantageous to generate it via flash vacuum pyrolysis (FVP) followed by trapping in an inert matrix rather than by photolysis of a matrix-isolated precursor. In the latter case radical pairs are formed in the same matrix cage, and annealing of the matrix results predominantly in recombination of these radical pairs rather than in reactions with other small molecules trapped in the matrix. In our hands the FVP of azobenzene 4 with subsequent trapping of the



Scheme 1. Reactions of the phenyl radical 2.

Table 1. IR spectroscopic data of two isotopomers of the benzoyl radical 1.



pyrolysis products in a large excess of argon at 15 K produced good yields of matrix-isolated 2.^[23,24] In addition to 2 the matrix contains benzene (formed from 2 via hydrogen abstraction), acetylene (from the thermal decomposition of 2) and unreacted starting material 4. If an argon matrix containing 2 is doped with small amounts of oxygen (0.5– 2%) radical 2 is easily trapped to give the phenylperoxy radical 5.^[24] This bimolecular reaction is induced by warming the matrix from 10 K to approximately 30 K, where the ridgid argon matrix is getting soft and diffusion of small trapped molecules becomes rapid. We therefore used similar conditions for the trapping experiments of 2 with CO.

Trapping of the products of the pyrolysis of **4** in argon doped with 2% CO at 10 K resulted in the formation of a new product with a strong IR band at 1824.4 cm⁻¹ that was not present in the absence of CO. If the matrix was annealed at 30-35 K, all IR bands assigned to the new product (Figure 1, Table 1) increased in intensity while that of the phenyl radical 2 decreased. This indicates that the new compound is formed by a bimolecular reaction between 2 and CO with a very low or absent activation barrier. It is tempting to assign the new IR band at 1824.4 cm⁻¹ to the C=O str. vibration of the benzoyl radical 1. This is confirmed by comparison with the transient IR spectrum of 1 obtained by time resolved IR spectroscopy.^[5] The C=O stretching vibration of **1** in argon at 1824.4 cm⁻¹ very nicely matches the corresponding absorption in CCl₄ at 1824 cm⁻¹. The assignment of the IR spectrum of 1 was further confirmed by comparison of the spectrum in solid argon with calculations at the UB3LYP/cc-pVTZ level of

	C ₆ H ₅ CO (1)		C ₆ D ₅ CO (d ₅ -1)		Assignment		
Mode ^[a]	Argon ^[b]	DFT ^[c]	Argon ^[b]	DFT ^[c]	Sym.		
28	1824.4 (100)	1886.2 (100)	1815.8 (100)	1885.9 (100)	\mathbf{A}'	C=O str.	
27	1594.8 (2)	1635.0 (6)	1556.8 (6)	1597.3 (6)	\mathbf{A}'	C=C str.	
26	1581.0 (9)	1619.0 (4)	1550.0 (8)	1579.3 (5)	\mathbf{A}'	C=C str.	
25	_	1518.8 (0)	1356.3 (<1)	1386.4 (1)	\mathbf{A}'	C-H def.(in plane)	
24	1450.3 (4)	1484.0 (5)	1327.1 (7)	1357.7 (3)	\mathbf{A}'	C-H def.(in plane)	
23	1307.8 (<1)	1354.6 (2)	_	1061.5 (0)	\mathbf{A}'	C-H def.(in plane)	
22	1288.0 (1)	1333.8 (2)	1297.0 (3)	1328.9 (3)	\mathbf{A}'	C-H def./C-C str (ring)	
21	_	1203.4 (0)	866.6 (<1)	884.1 (0)	\mathbf{A}'	C-H def.(in plane)	
20	_	1187.6 (0)	845.5 (2)	862.5 (1)	\mathbf{A}'	C-H def.(in plane)	
19	1136.2 (21)	1163.5 (21)	1100.1 (32)	1124.3 (13)	\mathbf{A}'	C-H def./C-C str.	
18	1070.4 (3)	1102.0 (2)	817.2 (≈ 1)	834.4 (1)	\mathbf{A}'	C-H def.(in plane)	
17	_	1048.6 (1)	831.5 (13)	850.8 (6)	\mathbf{A}'	C-H def.(in plane)	
16	_	1026.8 (0)	_	861.6 (0)	A''	C-H def.(out-of-plane)	
15	_	1022.2. (0)	959.6 (5)	978.8 (0)	\mathbf{A}'	ring str.	
14	_	1007.0 (0)	_	820.8 (0)	A''	C-H def.(out-of-plane)	
13	935.8 (2)	965.8 (1)	765.1 (3)	791.4 (1)	A''	C-H def.(out-of-plane)	
12	_	872.4 (0)	_	678.0 (0)	A''	C-H def.(out-of-plane)	
11	789.7 (11)	807.6 (5)	749.3 (6)	762.2 (3)	\mathbf{A}'	C–O str./ ring str.	
10	755.9 (12)	774.8 (18)	545.5 (27)	557.7 (11)	$A^{\prime\prime}$	C-H def.(out-of-plane)	
9	687.8 (10)	709.3 (10)	624.9 (2)	643.5 (2)	A''	C-H def.(out-of-plane)	
8	624.7 (16)	637.7 (4)	603.7 (15)	618.9 (5)	\mathbf{A}'	CCO def./ring str.	
7	610.4 (10)	625.9 (3)	587.0 (5)	602.0 (1)	\mathbf{A}'	CCO def./ring str.	
6	_	471.3 (1)	_	418.1 (2)	A''	C-H def.(out-of-plane)	
5	_	442.2 (0)	_	431.2 (0)	\mathbf{A}'	CCC def.	
4	_	418.7 (0)	_	363.5 (0)	A''	C-H def.(out-of-plane)	

[a] Mode numbers based on the $C_6H_5^{12}C^{16}O$ isotopomer. [b] Argon matrix at 10 K. Wavenumbers in cm⁻¹ and relative intensities in parenthesis. [c] Calculated at the UB3LYP/cc-pVTZ level of theory.

theory, which nicely reproduce the experimental spectrum (Table 1). If d_5 -2 is used the corresponding d_5 -1 is formed with the expected IR spectrum (Figure S1).



Figure 1. IR spectra showing the annealing of an argon matrix doped with 1% CO containing phenyl radical **2**. The band at 1824.4 assigned to **1** is growing in intensity during warming the matrix. (a) Matrix at 10 K (b) The same matrix after annealing at 25 K for 10 min, (c) after annealing at 30 K for 10 min, and (d) after annealing at 35 K for 10 min.

According to DFT calculation the reaction $2 + CO \rightarrow 1$ is exothermic by 24.58 kcal/mol with a barrier of 0.7 kcal/ mol at the B3LYP and 3.3 kcal/mol at the MP2 level of theory.^[10] The reaction between 2 and CO in solid argon is rapid at temperatures above 30 K where the diffusion of small molecules in argon becomes possible. From that we conclude that the thermal barrier for this reaction must be very small or absent, in agreement with the theoretical predictions. The formation of **1** from **2** and CO is photochemically reversible. Irradiation of matrix-isolated **1** at 10 K with UV light ($\lambda > 260$ nm) leads back to **2** and CO (Figure 2). Subsequent annealing at 35 K again results in the formation of **1**.

The Benzoylperoxy Radical

In solution, the benzoyl radical 1 can be trapped by molecular oxygen to produce the benzoylperoxy radical 3.^[5] Under the conditions of matrix isolation the formation of 3 requires that the phenyl radical 2 first reacts with CO to give 1, which in a second thermal step reacts with O_2 to give 3. Both thermal steps depend on the diffusion of CO and O_2 , respectively, in the solid matrix. Since 2 is also highly reactive towards oxygen, mixtures of 3 and the phenylperoxy radical 5 are expected to be formed if mixtures of CO and O_2 are used as trapping reagents in argon. To increase the yield of 3 we therefore used an excess of CO with respect to O_2 in the experiments.

If an argon matrix containing **2** doped with ca. 0.5% O₂ and 2% CO is slowly warmed from 10 K to 35 K the formation of 1 as the primary product and 5 as a minor product can be monitored by IR spectroscopy. However, 1 is also trapped by O₂ and during continuous warming of the matrix all IR bands assigned to 1 decrease in intensity and a new product with a prominent C=O str. vibration at 1820.9 cm⁻¹ is formed. If ¹⁸O₂ is used in the experiment this band is almost not effected, indicating that the oxygen atom of the C=O bond comes from CO and not from O_2 (Figure 3, Table 2). Large ¹⁸O isotopic shifts are found for a band at 1107.0 cm^{-1} (-68.1 cm⁻¹) and 768.2 cm⁻¹ (-21.6 cm^{-1}) which are thus assigned to O–O and a C–O stretching vibrations, respectively. For the transient benzoylperoxy radical 3 in CCl₄ a C=O stretching vibration of 1820 cm⁻¹ was reported,^[5] in excellent agreement with the



Figure 2. Difference IR spectra showing the photochemistry ($\lambda > 350$ nm) of 1, matrix-isolated in argon at 10 K. Bands pointing downwards are disappearing during irradiation and assigned to 1. Bands pointing upwards are appearing and assigned to 2. (a) IR spectrum of 1 calculated at the UB3LYP/cc-pVTZ level of theory. (b) Difference IR spectrum after 30 min irradiation. (c) IR spectrum of 2 calculated at the UB3LYP/cc-pVTZ level of theory.



band found in the CO/O_2 trapping experiment. We therefore assign the new compound formed only in the presence of both CO and O_2 to radical **3** (Figure 4).



Figure 3. IR spectra showing the annealing of an argon matrix doped with 2% CO and 0.5% O₂ containing phenyl radical **2**. The matrix was slowly (approximately 1 K/min) warmed from 10 K (t = 0 min) to 40 K (t = 30 min). The band at 1824 cm⁻¹ is assigned to benzoyl radical **1** and the band at 1820.9 cm⁻¹ to benzoylperoxy radical **3**.

The band positions, relative intensities, and isotopic shifts of **3** (18 O and d₅ isotopomers) are in good agreement with predictions from DFT calculations at the UB3LYP/cc-

pVTZ level of theory (Figures S4 and S5, Table 2). These experiments clearly show that the thermal reaction of **2** with CO can compete with the reaction with O_2 and that the benzoyl radical **1** rapidly reacts with molecular oxygen. DFT calculations do not indicate an activation barrier for the oxygen trapping of **1** (Figure S2).

Two rotamers **3a** and **3b** are possibly formed in the experiments. According to UB3LYP/cc-pVTZ calculations the s-Z conformer **3a** is by 3.47 kcal/mol (ZPE = 3.31 kcal/mol) more stable than the s-*E* conformer **3b**. The activation barrier for the **3a** \rightarrow **3b** isomerization is calculated to 5.03 kcal/mol (Figure S3). The calculated IR spectrum of **3a** is in good agreement with the experimental spectrum of **3a**, and there is no evidence for the formation of the less stable conformer **3b**.

UV irradiation ($\lambda > 260$ nm) of **3** at 10 K results in the disappearance of all bands assigned to **3** and formation of CO₂ and several other new bands, in particular several strong and broad absorptions in the range between 2140 and 2120 cm⁻¹. If ¹⁸O₂/¹⁶O₂ mixtures are used in the experiment new bands around 2089 cm⁻¹ appear, which clearly indicates that one or several ketenes are formed. In addition, the three isotopomers C¹⁶O₂, C¹⁸O¹⁶O, and C¹⁸O₂ are found (Figure S6). We assume that the photolysis of **3** results in ring-opening and formation of ketenes. However, due to the low intensity of other IR bands of the ketenes (presumably several isomers or conformers are formed) a definitive assignment was not possible.

Table 2. IR spectroscopic data of four isotopomers of the benzoylperoxy radical 3.

Mode ^[a]	$[a] C_6H_5CO^{16}O^{16}O(3)$		C ₆ H ₅ CO ¹⁸ O ¹⁸ O (3)		C ₆ D ₅ CO ¹⁶ O ¹⁶ O (3)		C ₆ D ₅ CO ¹⁸ O ¹⁸ O (3)		Assignment
34	1820.9 (100)	1868.2 (100)	1820.6 (100)	1867.9 (100)	1821.1 (100)	1867.8 (100)	1821.3 (100)	1867.6 (100)	C=O str.
33	1603.0 (10)	1643.1 (12)	1601.7 (13)	1643.1 (12)	1567.1 (22)	1605.1 (15)	1567.2 (48)	1605.1 (15)	C=C str.
32	_	1622.0 (1)	_	1622.0 (1)	_	1583.4 (1)	-	1583.4 (1)	C=C str.
31	_	1529.1 (0)	_	1529.1 (0)	1378.3 (10)	1404.8 (8)	1377.8 (20)	1404.6 (8)	C-H def.
30	1455.8 (<1)	1487.6 (6)	1455.2 (<1)	1487.6 (6)	1333.4 (5)	1364.0 (5)	1333.3 (12)	1363.9 (5)	C-H def.
29	_	1362.0 (2)	1322.7 (<1)	1362.0 (2)	1042.7 (3)	1066.3 (2)	1042.9 (4)	1064.8 (4)	C-H def.
28	_	1341.2 (1)	1309.8 (<1)	1340.9 (1)	1300.2 (4)	1336.6 (2)	1299.8 (8)	1336.5 (2)	C-H def./C-C str
27	1228.4 (38)	1247.8 (53)	1225.8 (63)	1246.6 (57)	1174.7 (49)	1195.6 (41)	1174.4 (54)	1192.8 (41)	C-C str./ C-H def.
26	1183.8 (8)	1206.6 (13)	1183.1 (10)	1206.6 (14)	866.8 (9)	883.4 (5)	866.7 (22)	883.3 (5)	C-H def.
25	_	1189.9 (0)	_	1189.9 (0)	846.2 (1)	862.7 (1)	846.6 (6)	862.6 (1)	C-H def.
24	1107.0 (7)	1155.2 (19)	1038.9 (8)	1090.6 (12)	1106.3 (12)	1154.0 (29)	1033.4 (18)	1092.2 (12)	O–O str.
23	_	1112.6 (1)	_	1112.7 (1)	824.3 (4)	842.3 (1)	824.3 (10)	842.2 (2)	C-H def.
22	_	1053.0 (0)	_	1052.9 (0)	-	839.2 (3)	813.7 (5)	838.7 (3)	C-H def.
21	_	1028.5 (0)	_	1028.5 (0)	_	867.6 (0)	-	867.6 (0)	C–H wag.
20	1002.3 (3)	1022.2 (1)	1002.3 (3)	1022.2 (1)	959.8 (7)	978.6 (1)	959.7 (14)	978.5 (1)	C–C str. (ring)
19	-	1008.9 (0)	-	1008.9 (0)	-	822.7 (0)	-	822.7 (0)	C–H wag.
18	_	973.0 (1)	950.3 (<1)	973.0 (1)	_	815.3 (0)	_	815.2 (0)	C-H wag.
17	935.8 (65)	948.7 (57)	934.4 (67)	946.6 (58)	927.2 (60)	941.2 (49)	926.0 (98)	939.3 (49)	C–O str.
16	_	870.9 (0)	_	870.9 (0)	_	677.2 (0)	-	677.2 (0)	C–H wag.
15	783.6 (5)	807.5 (4)	788.5 (2)	807.3 (4)	701.7 (3)	719.6 (2)	701.6 (4)	719.0 (2)	C-H wag.
14	768.2 (10)	772.7 (28)	746.6 (10)	748.9 (28)	762.8 (9)	768.0 (26)	740.7 (12)	742.7 (24)	C–O str.
13	692.5 (27)	710.5 (25)	692.3 (20)	710.4 (24)	536.4 (14)	548.0 (16)	536.4 (32)	547.9 (16)	C–H wag.
12	678.6 (11)	694.7 (5)	678.6 (5)	690.0 (3)	651.8 (10)	666.8 (5)	648.9 (10)	663.9 (4)	ring skel.
11	668.5 (8)	687.2 (7)	668.2 (7)	686.4 (7)	604.0 (2)	620.6 (3)	604.4 (6)	620.2 (3)	ring out of plane
10	_	631.7 (1)	_	631.6 (1)	590.9 (<1)	605.5 (0)	591.2 (2)	605.5 (0)	ring skel.
9	_	462.2 (1)	_	456.2 (1)	_	452.0 (1)	-	446.1 (1)	C-C-O def.
8	_	443.2 (0)	_	442.8 (0)	_	398.8 (0)	_	398.5 (0)	ring out of plane

[a] Mode numbers based on the $C_6H_5^{12}C^{16}O^{16}O^{16}O$ isotopomer.



Figure 4. Difference IR spectra showing the photochemistry ($\lambda > 260 \text{ nm}$) of 3, matrix-isolated in argon at 10 K. Bands pointing downwards are disappearing during irradiation and assigned to 3. (a) IR spectrum of 3 calculated at the UB3LYP/cc-pVTZ level of theory. (b) Difference IR spectrum after 60 min irradiation.

Conclusions

The phenyl radical is a highly reactive species that even under the conditions of matrix isolation rapidly reacts with CO and O_2 as long as diffusion of these small molecules in the solid matrix is possible. With CO the benzoyl radical 1 is formed which could be isolated and spectroscopically characterized. Interestingly, conditions could be found were mixtures of CO and O2 in the same matrix produce good yields of the benzoylperoxy radical 3 by subsequent reactions of the phenyl radical 2 with CO and O_2 . Obviously, the reaction of 2 with CO can compete with the reaction with O₂. This is in line with DFT and ab initio calculations which predict very shallow or absent activation barriers for both reactions. The formation of the radicals 1 and 5 in argon matrices depends on the statistical distribution and rates of diffusion of CO and O₂. An excess of CO compared to O_2 thus results in the preferential formation of 1 which subsequently reacts with O_2 to 3.

Experimental Section

Azobenzene and [D₁₀]Azobenzene: Azobenzene 4 (Acros Organics 99.8%) was used without further purification. The perdeuterated azobenzene d₁₀-4 was synthesized according to a literature procedure.^[25] ¹³C NMR (50.33 MHz, CDCI₃, 25 °C, TMS): δ_C = 152.99, 78.06, 77.43, 76.79. MS (RI, 70 eV): *m/z*, % 192 [M⁺], 110, 82, 54, 45.

Matrix Isolation: Matrix isolation experiments were performed by standard techniques^[26] using a closed cycle helium cryostat and a CsI spectroscopic window cooled to 10 K. FTIR spectra were recorded with a standard resolution of 0.5 cm^{-1} , using a N₂(l)-cooled MCT detector in the range 400–4000 cm⁻¹. UV spectra were recorded between 800 and 200 nm with a standard resolution of 0.02 nm (Varian UV/Vis NIR spectrophotometer) from a sample deposited on a sapphire window cooled to 10 K by a closed-cycle cryostat. Flash vacuum pyrolysis was carried out by slowly subliming azobenzene **4** through a 7 cm quartz tube heated electrically with a tantalum wire. Broadband irradiation was carried out with mercury high-pressure arc lamps in housings equipped with quartz

optics and dichroic mirrors in combination with cutoff filters (50% transmission at the wavelength specified).

Computational Methods: Optimized geometries and vibrational frequencies of all species were calculated at the UB3LYP^[27–29] level of theory using the 6-311+G(d,p) polarized valence-triple- ξ basis set^[30,31] and Dunning's cc-pVTZ basis sets.^[32–34] All DFT calculations were carried out with Gaussian 03.^[35]

Acknowledgments

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) and the Fond der Chemischen Industrie.

- N. S. Allen, M. C. Marin, M. Edge, D. W. Davies, J. Garrett, F. Jones, S. Navaratnam, B. J. Parsons, J. Photochem. Photobiol. 1999, 126, 135.
- [2] A. Ajayaghosh, S. Das, M. V. George, J. Polym. Sci., Part A: Polym. Chem. 1993, 31, 653.
- [3] J. Eichler, C. P. Herz, I. Naito, W. Schnabel, J. Photochem. 1980, 12, 225.
- [4] C. P. Herz, J. Eichler, Farbe Lack 1979, 85, 933.
- [5] C. Kolano, G. Bucher, H. H. Wenk, M. Jaeger, O. Schade, W. Sander, J. Phys. Org. Chem. 2004, 17, 207.
- [6] C. S. Colley, D. C. Grills, N. A. Besley, S. Jockusch, P. Matousek, A. W. Parker, M. Towrie, N. J. Turro, P. M. W. Gill, M. W. George, J. Am. Chem. Soc. 2002, 124, 14952.
- [7] G. W. Sluggett, P. F. McGarry, I. V. Koptyug, N. J. Turro, J. Am. Chem. Soc. 1996, 118, 7367.
- [8] R. K. Solly, S. W. Benson, J. Am. Chem. Soc. 1971, 93, 2127.
- [9] G.-J. Nam, W. Xia, J. Park, M. C. Lin, Chem. Phys. Processes Combust. 1999, 304.
- [10] G.-J. Nam, W. Xia, J. Park, M. C. Lin, J. Phys. Chem. A 2000, 104, 1233.
- [11] P. J. Krusic, T. A. Rettig, J. Am. Chem. Soc. 1970, 92, 722.
- [12] J. E. Bennett, B. Mile, Trans. Faraday Soc. 1971, 67, 1587.
- [13] O. Ito, T. Sakaguchi, M. Matsuda, J. Chem. Soc. Faraday Trans. 1978, 74, 1188.
- [14] C. E. Brown, A. G. Neville, D. M. Rayner, K. U. Ingold, J. Lusztyk, Aust. J. Chem. 1995, 48, 363.
- [15] J. A. Martinho Simoes, D. Griller, Chem. Phys. Lett. 1989, 158, 175.
- [16] A. G. Neville, C. E. Brown, D. M. Rayner, J. Lusztyk, K. U. Ingold, J. Am. Chem. Soc. 1991, 113, 1869.
- [17] M. Hoshino, R. Konishi, H. Seto, H. Seki, H. Sonoki, T. Yokoyama, H. Shimamori, *Res. Chem. Intermed.* 2001, 27, 189.

- [18] A. G. Merzlikine, S. V. Voskresensky, E. O. Danilov, D. C. Neckers, A. V. Fedorov, *Photochem. Photobiol. Sci.* 2007, 6, 608.
- [19] L. Grossi, G. Placucci, J. Chem. Soc., Chem. Commun. 1985, 943.
- [20] J. Pacansky, J. Bargon, J. Am. Chem. Soc. 1975, 97, 6896.
- [21] J. G. Radziszewski, M. R. Nimlos, P. R. Winter, G. B. Ellison, J. Am. Chem. Soc. 1996, 118, 7400.
- [22] A. V. Friderichsen, J. G. Radziszewski, M. R. Nimlos, P. R. Winter, D. C. Dayton, D. E. David, G. B. Ellison, J. Am. Chem. Soc. 2001, 123, 1977.
- [23] A. Mardyukov, E. Sanchez-Garcia, R. Crespo-Otero, W. Sander, Angew. Chem. Int. Ed. 2009, 48, 4804.
- [24] A. Mardyukov, W. Sander, Chem. Eur. J. 2009, 15, 1462.
- [25] H. E. Bigelow, D. B. Robinson, Org. Synth. 1942, 22, 28.
- [26] I. Dunkin, Matrix Isolation Techniques: A Practical Approach, 1998.
- [27] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [28] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785.
- [29] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 1989, 157, 200.
- [30] A. D. McLean, G. S. Chandler, J. Chem. Phys. 1980, 72, 5639.
- [31] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. 1980, 72, 650.

- [32] D. E. Woon, T. H. Dunning Jr., J. Chem. Phys. 1993, 98, 1358.
- [33] R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, J. Chem. Phys. 1992, 96, 6796.
- [34] T. H. Dunning Jr., J. Chem. Phys. 1989, 90, 1007.
- [35] G. W. T. M. J. Krishnan, H. B. Schlegel, G. E. Scuseria, J. R. C. M. A. Robb, J. A. Montgomery Jr., T. Vreven J. C. B. K. N. Kudin, J. M. Millam, S. S. Iyengar, J. Tomasi, B. M. V. Barone, M. Cossi, G. Scalmani, N. Rega, H. N. G. A. Petersson, M. Hada, M. Ehara, K. Toyota, J. H. R. Fukuda, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, M. K. H. Nakai, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, J. J. C. Adamo, R. Gomperts, R. E. Stratmann, O. Yazyev, R. C. A. J. Austin, C. Pomelli, J. W. Ochterski, P. Y. Ayala, G. A. V. K. Morokuma, P. Salvador, J. J. Dannenberg, S. D. V. G. Zakrzewski, A. D. Daniels, M. C. Strain, D. K. M. O. Farkas, A. D. Rabuck, K. Raghavachari, J. V. O. J. B. Foresman, Q. Cui, A. G. Baboul, S. Clifford, B. B. S. J. Cioslowski, G. Liu, A. Liashenko, P. Piskorz, R. L. M. I. Komaromi, D. J. Fox, T. Keith, M. A. Al-Laham, A. N. C. Y. Peng, M. Challacombe, P. M. W. Gill, W. C. B. Johnson, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, rev. B.1, Pittsburgh, PA, 2003.

Received: February 3, 2010 Published Online: April 14, 2010